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TSPC/DC MEASUREMENTS ON BARIUM TITANATE

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Abstract

Thermally-stimulated polarization/depolarization current (TSPC/DC) measurements were made on high-purity doped and undoped $BaTiO_3$ as a function of applied field, heating rate, dopant level, and Ba:Ti ratio. The form of the TSPC/DC curves is dependent upon both the resistive and ferroelectric properties of $BaTiO_3$. For TSPC spectra, current peaks are exhibited due to the change in in magnitude and direction of the spontaneous polarization with changing crystal structure. In particular, whether the phase transition is first or second order influences the existence and magnitude of the current peaks.

TSDC measurements are essentially dynamic pyroelectric measurements and as such are useful in determining the pyroelectric coefficient and the magnitude of the spontaneous polarization. The TSDC current did not approach zero in the paraelectric region for some of the specimens, indicative of an anomalous polarization present due to the migration of charged oxygen vacancies. This information is useful for analyzing DC electrical degradation.

Variation in the Ba:Ti ratio affects the grain size distribution, and hence, the ease of domain switching. This directly affects the presence and magnitude of current peaks. The Ba:Ti ratio also affects the activation energy of conduction, resistivity, and degradation behavior, all of which are reflected by the magnitude of the TSPC/DC current in the paraelectric region.

Introduction

In thermally-stimulated processes, a particular property of a material is measured as a function of temperature, usually from a "low" temperature which freezes in processes of interest. The system of interst usually exists in a non-equlibrium state (ie: poled), which is achieved by excitation at the low temperature or during cooling. Specifically, TSC measurements involve monitoring the current passing through a material subjected to a DC stress during heating.

TSPC/DC measurements have been extensively used for studying charge transport in in insulators.[1-6] Alkali motion and dipolar relaxation times in glasses[1], vacancy dipole reorientation in halides[2], point defect energy levels in insulators[3], and energy levels of trapping and recombination centers in semiconductors[4] have all been characterized by TSPC/DC techniques. Chen[5] and Braunlich[6] provide complete reviews of past uses of TSC measurements. The purpose of this study was to determine if TSPC/DC measurements would be useful in the study of ferroelectric materials.

Experimental Procedure

The $BaTiO_3$ powders utilized in this study were prepared by an organometallic technique[7]. Disc specimens were pressed and subsequently sintered in air at various temperatures and times in order to precisely control the microstructure. All discs were electroded using an unfritted platinum paste.

The apparatus used for the TSPC/DC and dielectric measurements is shown in Figure 1. It consists of an atmosphere-controlled, stainless steel chamber which houses a removable inner core assembly. Heating tape wrapped around the bottom of the tube and connected to a Eurotherm 211 controller allows precise control of the heating rate. A computer-controlled HP 4140 picoammeter/DC voltage source was used for current monitoring. Current sensitivity for the system was 10^{-14} amps. Capacitance and dissipation factor data were collected at 1 kHz using a General Radio 1689 RLC digibridge.

Figure 2 illustrates the sequence used for the TSC measurements, and is described as follows:

1. 1st Polarization: After a vacuum bake-out at 165°C and cooling to -100°C, a voltage was applied to the specimen, and the current monitored during heating at a constant rate. Monitored temperature range was from -100 to 165°C. This current spectra is denoted TSPC-1.

2. 2nd Polarization: After the first polarization, the specimen was immediately

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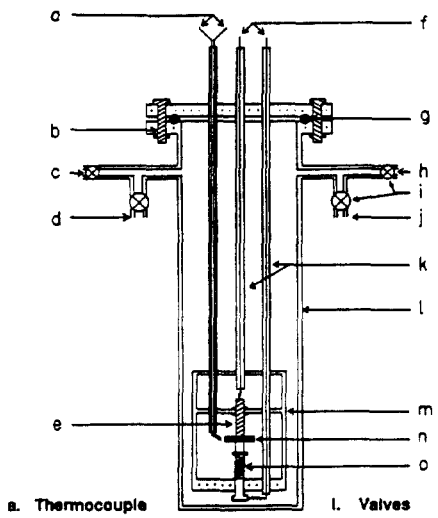
quenched to -100°C with the field applied. The now poled specimen was then heated and the current monitored as in TSPC-1. This current spectra was denoted TSPC-2.

3. Depolarization: Following TSPC-2, the specimen was quenched to -100°C with the field applied. At this point the field was removed, and the current monitored during heating as before. This current spectra was denoted TSDC.

Heating rates varied from 2.0 to 8.0°K/minute, and applied fields ranged from 250-2000 V/cm.



a. Thermocouple
b. Chamber Bolt
c. Exhaust
d. Vacuum Supply
e. Set Screw
f. Platinum Leads
g. O-ring
h. Helium Inlet
l. Valves
j. Vacuum Supply
k. Al_2O_3 Tubes
l. Stainless Steel Chamber
m. Support Frame
n. Specimen
o. Spring-Loaded Screw

Figure 1: TSPC/DC measurement apparatus.

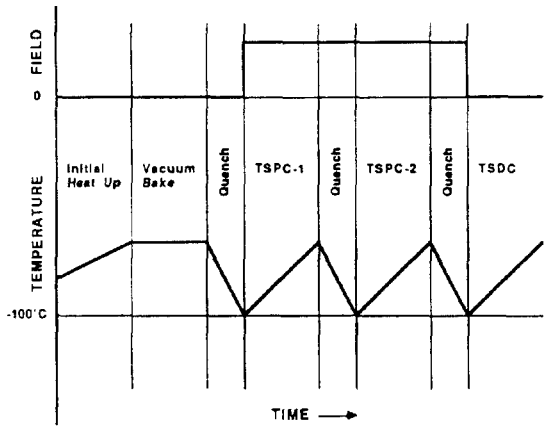


Figure 2: TSPC/DC measurement sequence.

Results and Discussion

The TSPC/DC behavior is plotted as +/- log current density versus temperature. Positive current corresponds to resistive currrent, ie: electron flow towards the anode. Negative current corresponds to electron flow in the opposite direction, indicative of the charging or displacement current which flows during polarization of the ferroelectric. In a TSPC experiment then, the total current flowing at any time is:

$$J_T(T) = J_D(T) + J_R(T) \qquad (1)$$

where $J_T(T)$, $J_D(T)$, and $J_R(T)$ are the total, displacement, and resistive current densities respectively. During a TSDC experiment, no field is applied and the current density becomes:

$$J_D = \frac{dP_S}{dt} = \frac{dP_S}{dT}\,\frac{dT}{dt} \qquad (2)$$

where dP_S/dT is the change in spontaneous polarization with temperature (the pyroelectric coefficient), and dT/dt is the heating rate. From a TSDC measurement the spontaneous polarization is determined from:

$$P_S = \int J_D(T)\,\frac{dT}{dt}\,dT \qquad (3)$$

Figures 3 and 4 contain the dielectric and TSPC/DC behavior for a stoichiometric $BaTiO_3$ specimen with a grain size of 10 microns and 96% theoretical density. The dielectric constant exhibits typical behavior, with maxima at the three phase transitions. TSPC-1 initially exhibits positive current in the rhombohedral region; the dipoles are "frozen-in" and unable to align with the field. As the specimen undergoes a phase transition to orthorhombic symmetry a peak is observed, the magnitude of which is proportional to the change in spontaneous polarization and the degree of poling whch occurs for a poling field of 1000 V/cm. A transition to positive current occurs as the resisitive component of the current again dominates, with a similiar current reversal and peak at the orthorhombic-tetragonal phase transition.

The behavior of the TSPC curve is of particular interest at the Curie temperature. Specimens with first order ferroelectric-paraelectric transitions exhibit a large negative peak as the spontaneous polarization changes discontinuously to zero. A specimen undergoing a second order transition does not exhibit a peak, as the Ba:Ti=1.005 specimen in Figure 5; the spontaneous polarization changes

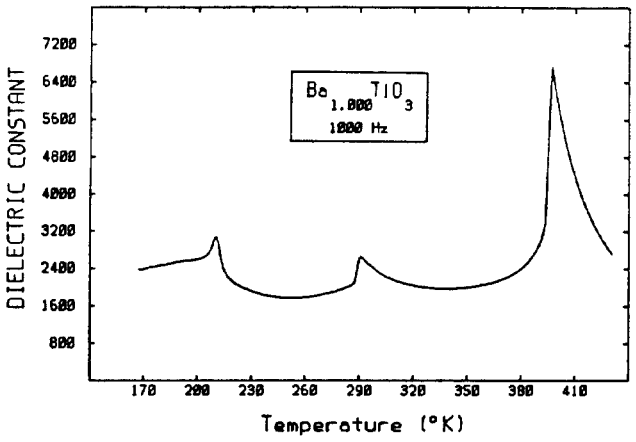


Figure 3: Dielectric constant of stoichiometric $BaTiO_3$.

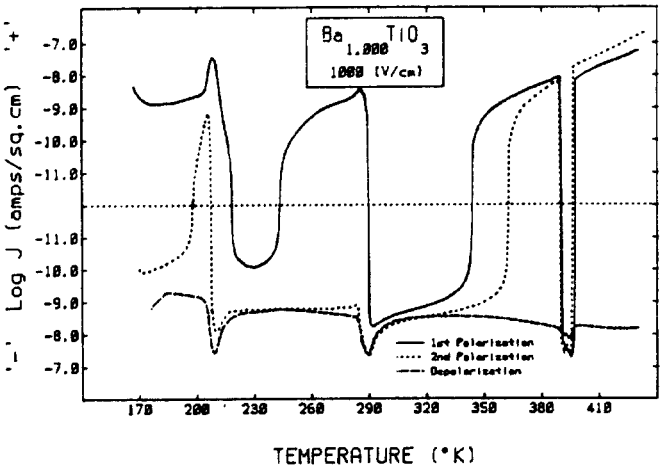


Figure 4: TSPC/DC spectra of stoichiometric $BaTiO_3$.

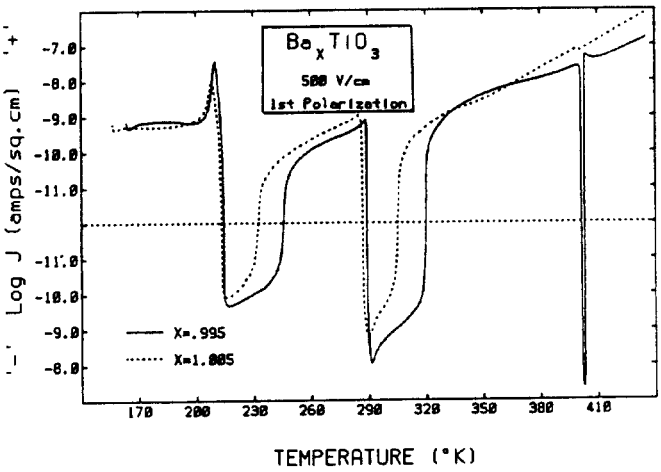


Figure 5: Comparison of TSPC-1 spectra for Ba:Ti = .995 and 1.005.

continuously to zero. Figure 6 summarizes this behavior.

The magnitude of TSPC-1 in the paraelectric region is proportional to the resistivity of the material, $\rho(T)$, which is found by dividing the applied field by the current density. The change in current density with temperature is exponentially proportional to the activation energy of conduction, which can be calculated assuming Arrhenius behavior. The activation energy for the $BaTiO_3$ specimen of Figure 4 is 1.0 eV, which agrees well with published data. This activation energy is composed of both the carrier concentration and mobility terms.

The TSPC-2 of Figure 4 is similiar to that of TSPC-1, but reflects the fact that the specimen is already in a poled state prior to heating.

The TSDC spectra contained in Figures 4,7 and 8 simply reflect the pyroelectric nature of $BaTiO_3$. Dividing the current density by the heating rate yields the pyroelectric coefficient. These results agree well with those published earlier by Perls et.al[7] for polycrystalline $BaTiO_3$. Figure 8 exhibits the degree of poling achieved for fields from 250-2000 V/cm. Increasing the poling field not only increases the discharge current during depolarization, but also decreases the temperature at which the orthorhombic-tetragonal phase transition occurs (Figure 9).

Figure 10 contains the TSDC spectra of excess barium compositions which exhibit DC electrical degradation at 500 V/cm[8]. Increasing the amount of excess barium increases the degradation rate, which is believed to be due to charged oxygen vacancy migration. The accumulation of oxygen vacancies at the cathode results in a quasi- space charge accumulation referred to as an anomalous polarization. This

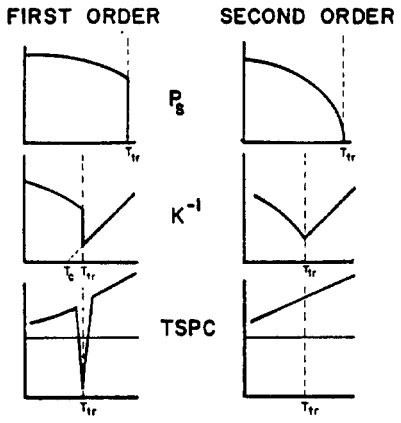


Figure 6: Variation of the spontaneous polarization and its affect on TSPC and inverse susceptibility.

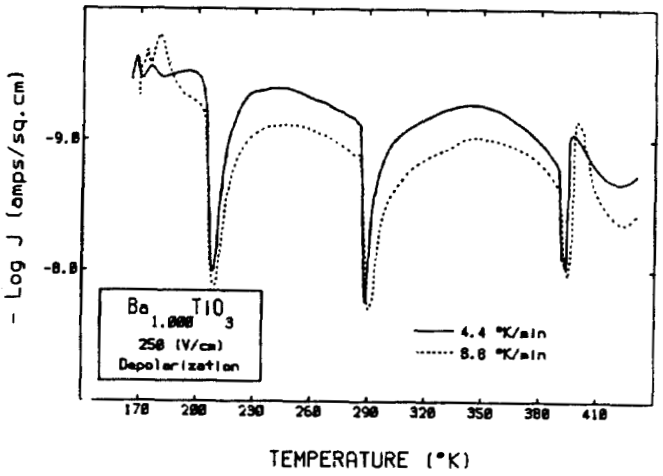


Figure 7: TSDC behavior of $BaTiO_3$ as a function of heating rate.

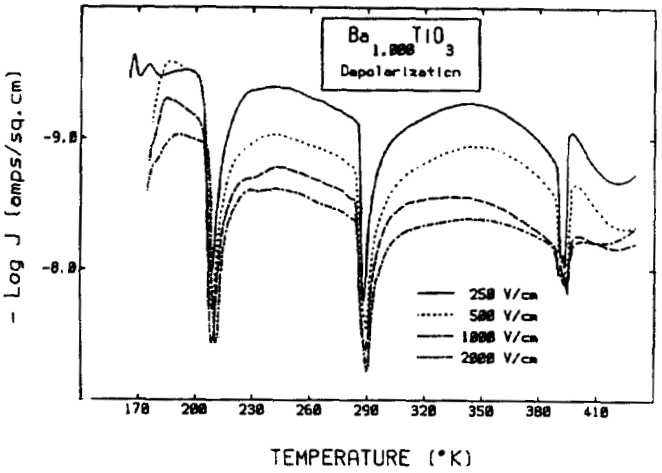


Figure 8: TSDC behavior of $BaTiO_3$ as a function of applied poling field.

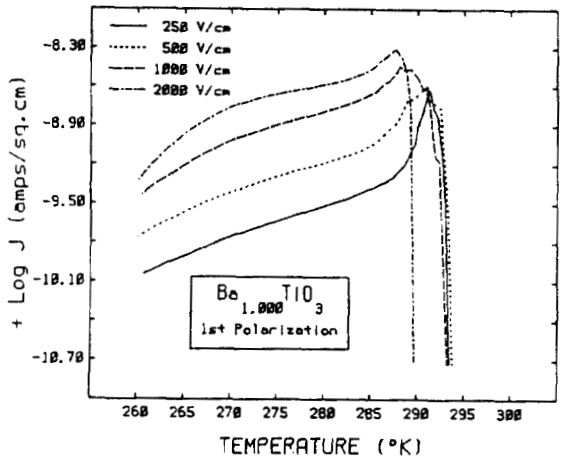


Figure 9: TSPC behavior at the orthorhombic-tetragonal phase transition as a function of appied field.

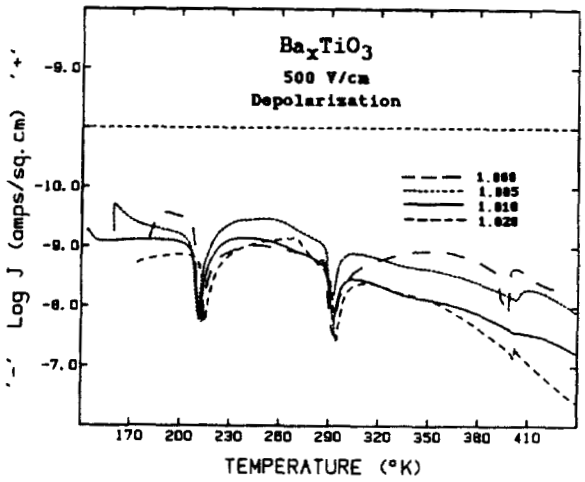


Figure 10: TSDC behavior of excess barium compositions.

effect is clearly illustrated in Figure 10; the pyroelectric current does not approach zero as expected in the paraelectric region. Instead the current continues to increase, the effect being larger in those specimens more prone to degradation.

Conclusions

TSPC/DC measurements are useful in characterizing the properties of ferroelectric materials. Pyroelectric coefficients and the spontaneous polarization are easily obtained from the TSDC spectra, while the TSPC spectra are useful in the analysis of phase transitions and domain switching. The purpose of this paper was to present the characteristic results one obtains in TSPC/DC measurements, and is by no means complete in terms of quantitative analysis. A full treatment of the mathematical aspects and background may be found elsewhere[9].

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